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Preparation and testing of cesium Brønsted ion-exchanged Al-SBA-15 supported heteropoly acid as heterogeneous catalyst in the fructose fragrant synthesis

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Abstract

Here we reported a new cesium Brønsted ion-exchanged Al-SBA-15 (AS15) supported heteropoly acid (HPA) $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPA-Cs/AS15) material which can be prepared and used as heterogeneous catalyst for the fructose fragrant synthesis. It was demonstrated that Cs^+ was more effective than NH_4^+ as counter cation of ion-exchanged AS15 support for preparing HPA/AS15 catalyst with higher acidity and HPA leaching stability. HPA-Cs/AS15 material showed high acidity with the maximum NH_3 desorption peak appeared at 759.6°C in NH_3 -TPD spectrum, stronger than pure HPA (635.7°C) and the ammonium Brønsted ion-exchanged Al-SBA-15 supported HPA (HPA- NH_4 /AS15) (559.1°C) materials. The HPA leaching stability test showed that the HPA content of HPA-Cs/AS15 catalyst reduced only 2.55 % after five washing times, much less than that of HPA- NH_4 /AS15 catalyst (49.22 %).

The higher acidity helped improve the HPA-Cs/AS15 catalyst performance in the fructose fragrant synthesis. The ethyl acetoacetate conversion over this catalyst was 94.82 %, better than those over HPA-

NH₄/AS15 (93.49 %) and pure HPA (89.52 %) catalysts, although HPA-Cs/AS15 catalyst had lower HPA content (23.16 wt%) than HPA-NH₄/AS15 (24.28 wt%). In addition, it was shown that at the reaction conditions such as ethyl acetoacetate:ethanediol reactants molar ratio of 1:1.5, ethanediol used as the diol reactant, and toluene used as the solvent, the fructose fragrance synthesis reaction over HPA-Cs/AS15 catalyst reached the highest ethyl acetoacetate conversion (95.58 %). The toluene's boiling temperature of 110.6 °C can promote the dispersion and contact abilities of the reactants with HPA molecules presented inside the pores of HPA-Cs/AS15 catalyst.

Keywords: cesium counter cation, heterogenised HPA, HPA/Al-SBA-15, fructose.

1. Introduction

Fructose (also known as 2,4-dimethyl-2-ethylacetoacetate-1,2-dioxolan) is a synthetic apple fragrance synthesised from the acetalisation reaction of ethyl acetoacetate (EAA) and diols substances using acid catalysts. Because of the commonly known disadvantages related to homogeneous acid catalysts such as difficult to separate and recover from the products, not be able to reuse, highly corrosive, expensive durable reactors are required [1, 2], heterogeneous catalysts for fructose fragrance synthesis such as SO₃H-functionalised carbon [3], copolymer of *p*-toluenesulfonic acid and *p*-formaldehyde [4], mesoporous Al-SBA-15 [5] and ultra-stable Y zeolite supported heteropoly acid [6], and a type of ionic liquid catalyst as SO₃H-functionalized BAILs [7] have been developed for easy recovery and reuse. Among these effective studied catalysts, the heteropoly acid (HPA) in α -Keggin form (H₃PW₁₂O₄₀) has been of great interests due to the high acidity of this catalyst and its possibility to be heterogenised using various methods such as precipitation [8-12], hybridisation [13-16], dispersion [17-21], encapsulation [6, 22, 23], tethering [24-26] and grafting [27, 28]. It has been shown that precipitation of HPA with cesium metal cation can improve physical properties of the hybrid catalyst (*i.e.* Cs-HPA salt) including the increased specific surface area (130-135 m²/g compared to 3.1 m²/g in purely HPA) due to the formed microporous structure [2, 12]. However, it is noteworthy that this approach might lead to lowered acidity (simply because of protons lost during the salt formation) which is likely to hinder the activity of this catalyst. In addition, it is known that the size of an anion of HPA molecule in α -Keggin form is close to 1 nm [23] which is too negligible to Cs-HPA salt (with the size between 11.7 and 17.5 nm [8, 9, 12]). It is shown that there was an unnecessary aggregation of the salt molecules, that might result in

the reduction of HPA dispersibility. For this reason, immobilising the HPA catalyst on high specific surface area porous supports by tethering or grafting methods should be studied.

In our previous study, HPA was successfully immobilised on NH_4^+ Brønsted ion-exchanged Al-SBA-15 mesoporous support. The prepared catalyst showed high catalytic activity in fructose fragrant synthesis with high conversion of EAA (93.49 %) [29]. Recently, Mukai *et. al.* have shown that Cs^+ cation was even more effective than NH_4^+ as counter cation of the support for HPA immobilisation on zeolite Y microporous material in terms of HPA content and leaching stability [23]. However, the microporous structure of zeolite Y could limit the mass transfer of reactions, and the contact between HPA molecules formed in the supercages of the support with reactants. Chamack *et. al.* have reported the HPA immobilisation on mesoporous SBA-15 support which was prior impregnated on its surface with Cs_2CO_3 for oxidative desulfurization processes [30]. The mesoporous structure of SBA-15 could solve the mentioned limitations of microporous structure of zeolite Y. In this reaction, the oxidative catalyst was more effective than acidic catalyst. Moreover, the impregnation method has the disadvantage of the low dispersibility of Cs_2CO_3 on SBA-15 support. The accumulation of Cs^+ cations in support may conduct the loss of acidity of immobilised HPA as mentioned elsewhere above. In order to disperse Cs^+ uniformly on the surface of support and remain the H^+ of HPA molecule, the use of Al-SBA-15 support, which has Brønsted site locations ion-exchanged with Cs^+ cations, expects to form the Al-SBA-15 supported heteropoly acid catalyst with high acidity.

In this study, the cesium Brønsted ion-exchanged Al-SBA-15 (AS15) supported heteropoly acid (HPA-Cs/AS15) material was prepared to be used as heterogeneous catalyst for the fructose fragrant synthesis. The presence and content of immobilised HPA were characterised by Fourier-transform infrared spectroscopy (FTIR), small angle X-ray scattering (SAXS) and energy dispersive X-ray (EDX) methods. The effect of HPA immobilisation on the support physical properties was evaluated by nitrogen adsorption/desorption isotherms. Acidity comparison among the samples was performed by using temperature-programmed desorption of ammonia (NH_3 -TPD) method. The obtained products of the fructose fragrant synthesis reaction were analysed by gas chromatography (GC).

2. Experimental

2.1. Catalyst preparation

2.1.1. Chemicals

The chemicals for HPA-Cs/AS15 preparation were listed in Table S1.

2.1.2. Synthesis of AS15 support

The AS15 support (denoted as AS15-OX) was synthesised by the typical process shown in the procedure 1 (see the supplementary information document) with the structural directing agent P123 removed by H_2O_2 oxidative agent.

2.1.3. Preparation of HPA-Cs/AS15 material

The HPA-Cs/AS15 material was prepared by the method shown in previous study [29] using two steps below. Step 1- AS15-OX support was Brønsted ion-exchanged with Cs^+ cation by using CsCl 1.5 M solution. The ion exchange procedure was shown in procedure 2 (see the supplementary information document).

Step 2- HPA Brønsted immobilisation (procedure 3 in the supplementary information document).

2.1.4. Comparison of AS15 support treatment condition

AS15 support was P123 removed by another method of thermal decomposition to compare with the AS15-OX support that was P123 removed by H_2O_2 oxidative agent. The AS15 sample contained P123 was thermal treated at 550 °C for 6 h with ramp of 3 °C/min to get the AS15-CAL support.

The obtained support was Brønsted ion-exchanged with NH_4^+ cation according to the ion exchange procedure shown in procedure 2 (see the supplementary information document) using NH_4NO_3 1.5 M solution, and then supported HPA according to the procedure of HPA-Cs/AS15 catalyst preparation to get the HPA- NH_4 /AS15-CAL sample.

2.1.5. Comparison of counter cation for AS15 support

AS15-OX support was Brønsted ion-exchanged with NH_4^+ instead of Cs^+ cation and then supported HPA according to the steps of HPA-Cs/AS15 catalyst preparation to obtain the HPA- NH_4 /AS15 sample. The AS15 supported HPA (HPA/AS15) samples were listed in Table 1.

2.2. Characterisation

EDX spectroscopy, SAXS diffraction patterns, nitrogen adsorption and desorption isotherms, NH_3 -TPD spectrums and FTIR spectrums of the samples were analysed on the equipments with the conditions shown in the supplementary information document.

2.3. Catalytic activity

Performance of the prepared HPA/AS15 samples was evaluated in the acetalisation reaction to synthesise fructose fragrance. The typical procedure was described in the previous study [29]. The reaction conditions were studied including solvent type (toluene, isooctane, cyclohexane), catalyst weight (2, 3, 4 wt% to reactants total mass); molar ratio of acetoacetate:ethanediol (EAA:EG) reactants (1:1, 1:1.25, 1:1.5, 1:1.75).

The homogeneous catalysts such as *p*-toluenesulfonic acid monohydrate (PTSA) and sulfuric acid (H₂SO₄), and pure HPA were used to make an activity comparison to the HPA-Cs/AS15 catalyst. Weights of these catalysts were calculated to have the same H⁺ mole value.

The HPA/AS15 catalysts were reused for 4 cycles of the reaction to evaluate their catalytic stability by the procedure shown in the previous study [29].

3. Results and discussion

3.1. Catalyst characterisation

3.1.1. FTIR results

The presence of HPA on the AS15 support can be detected by FTIR spectrums (see Fig. 1). Typical peaks attributed to the W-O-W, W-O and P-O linkages of HPA can be seen at 802.14 cm⁻¹, 892.97 cm⁻¹ and 983.54 cm⁻¹, and 1080.71 cm⁻¹, respectively (see Fig. 1f). These peaks are also observed in FTIR spectrums of the HPA-NH₄/AS15-CAL (Fig. 1a), HPA-Cs/AS15 (Fig. 1b) and HPA-NH₄/AS15 (Fig. 1c) samples. The higher intensity of the peak observed at 805.67 in the FTIR spectrums of HPA/AS15 samples compared to those in the AS15 supports indicates the presence of W-O-W linkages of HPA beside the Si-O-Si(Al) linkages of AS15 support.

3.1.2. SAXS results

SAXS patterns of the samples are shown in Fig. 2. There is the appearance of the peaks near 2-theta of 0.5-1° attributed to mesoporous structure of all the samples [29-31]. The presence of HPA is evidenced by the considerable decrease of those peaks in SAXS patterns of the HPA-NH₄/AS15-CAL (Fig. 2a), HPA-Cs/AS15 (Fig. 2b) and HPA-NH₄/AS15 (Fig. 2c) samples.

It can be also observed that these peaks in the SAXS patterns of HPA-NH₄/AS15-CAL and HPA-Cs/AS15 samples are shifted to the left. This shift may be due to the enlargement of mesopore size conducted by a part

dissolution of framework Si and Al atoms in acidic HPA solution ($\text{pH} \approx 1.5$) during the HPA Brønsted immobilisation.

3.1.3. Nitrogen adsorption and desorption isotherms

The presence of HPA in the HPA/AS15 samples also can be further confirmed by N_2 adsorption and desorption isotherms. The shape transformations of hysteresis loops in isotherms of the samples shown in Fig. 3 indicate the change of pore characteristic of the samples before and after supporting HPA. The data shown in Table 2 indicate that there are the decreases of BET surface area (S_{BET}), average pore diameter (D_{pore}) and pore volume (V_{pore}) values of the HPA/AS15 samples compared with initial corresponding supports conducted by the influence of HPA molecules presented inside the pores of AS15 support.

A clear result can be observed in Fig. 4, there are the enlargements of pore diameter of the samples after the HPA Brønsted immobilisation. The pore sizes of AS15-OX (Fig. 4e) and AS15-CAL (Fig. 4d) samples are mainly 5.5 and 6.5 nm in diameter, respectively. After the HPA Brønsted immobilisation, HPA molecules entered into the pores of AS15 support create the smaller pore systems with 4.0 and 6.25 nm in diameter for the samples using AS15-OX support (HPA-NH₄/AS15 (Fig. 4c) and HPA-Cs/AS15 samples (Fig. 4b)) and AS15-CAL support (HPA-NH₄/AS15-CAL sample (Fig. 4a)), respectively.

Beside the smaller pore systems, the bigger pore systems are also observed with 6.5 nm for HPA-NH₄/AS15 samples (Fig. 4c) and 7.0 nm for HPA-NH₄/AS15-CAL sample (Fig. 4a) compared to the pore systems of the corresponding supports. The formation of these bigger pores systems agrees with the obtained XRD result. It helps to improve the specific surface area of the supports and be the reason of the slightly decreased S_{BET} values even with high immobilised HPA contents of the HPA/AS15 samples.

Especially, the observed bigger pore system of HPA-Cs/AS15 sample is 8.2 nm in diameter (Fig. 4b), even larger than that of HPA-NH₄/AS15 sample (6.5 nm) (Fig. 4c). The pore-size enlargement of HPA-Cs/AS15 sample may be due to the interaction between the strong base support (Cs^+ Brønsted ion-exchanged AS15) and the strong acid (HPA), conducting the D_{pore} and V_{pore} increases of this sample compared to HPA-NH₄/AS15-CAL sample.

3.2. Catalytic activity

3.2.1. Effect of support treatment condition

The AS15 support was synthesised by using structural directing agent (Pluronic - P123). This agent needs to be removed after the structure formation of AS15. The removal methods such as thermal treatment or using strong oxidation agent (H_2O_2) lead to the property difference of material. BET results of the samples shown in Table 2 and Fig. 4 indicate that HPA-NH₄/AS15-CAL sample (prepared using AS15-CAL support) has slightly higher S_{BET} , D_{pore} and V_{pore} values than HPA-NH₄/AS15 sample (prepared using AS15-OX support). However, EDX results shown in Table 3 indicate that HPA content of HPA-NH₄/AS15-CAL sample is only 17.81 wt%, lower than that of HPA-NH₄/AS15 sample (24.28 wt%). This results in the lower catalytic activity of HPA-NH₄/AS15-CAL sample compared to that of HPA-NH₄/AS15 sample in the fructose fragrant synthesis. Fig. 5 and the data shown in Table S2 indicate that ethylacetoacetate conversion (EAA conv.) over HPA-NH₄/AS15-CAL sample is 90.14 %, lower than that over HPA-NH₄/AS15 sample (EAA conv. is 93.49 %).

The different HPA contents of the samples with different support treatment conditions may be explained by the fact that Si/Al molar ratio of AS15 support is 15. During the thermal treatment at 550 °C to remove P123, two neighbouring Brønsted sites can react to each other to form one Lewis site by the reaction shown in Fig. 6 [32]. This reaction decomposes the Brønsted sites and make them malfunctioned. In this case, HPA cannot be immobilised on these malfunctioned Brønsted sites, leading to the lower HPA content and therefore lower catalytic activity of HPA-NH₄/AS15-CAL sample compared to that of HPA-NH₄/AS15 sample. This result shows that P123 structural agent removed by oxidation method using H_2O_2 agent is more suitable than that by thermal treatment method to synthesize AS15 support for HPA Brønsted immobilisation.

3.2.2. Effect of counter cation of AS15 support

Cs^+ and NH_4^+ have been well known as effective counter cations for HPA encapsulation in zeolites [2, 22, 23]. Mukai et.al. showed that Cs^+ cation was even better than NH_4^+ for HPA Brønsted immobilisation on zeolite Y support [23] with higher HPA content and better leaching stability in polar media. This result once again can be seen in the case of AS15 support. Mesoporous system of the AS15 support promotes the easy ion exchanges between counter cations (NH_4^+ and Cs^+) and Brønsted sites, resulting in the similar HPA contents of HPA-NH₄/AS15 (24.28 wt%) and HPA-Cs/AS15 (23.16 wt%) samples as can be seen in Table 3.

The fructose fragrant synthesis efficiency shown in Fig. 7 and Table S3 indicates that HPA-Cs/AS15 sample has slightly better EAA conversion (94.82 %) than HPA-NH₄/AS15 sample (93.49 %) even with slightly lower

HPA content. This result indicates that HPA-Cs/AS15 sample may have higher acidity than HPA-NH₄/AS15 sample. The NH₃-TPD analysis result shown in Fig. 8 can illustrate clearly this indication.

In comparison to the AS15-OX support with low acidity, the NH₃-TPD spectrums of HPA-NH₄/AS15 and HPA-Cs/AS15 samples indicate their much higher acidities by the appearance of NH₃ desorption peaks attributed to strong acid sites at high temperatures. In comparison to HPA sample (which has NH₃ desorption peak in the NH₃-TPD spectrum observed at 635.7 °C), HPA-NH₄/AS15 sample shows lower acidity (with the peak observed at 559.1°C), HPA-Cs/AS15 shows even higher acidity (with the peak appeared at 759.6°C). The different acidity of the samples shows that there is an effect of counter cation on the acidity of sample. Cs⁺ cation can promote the acidity of the HPA formed in HPA-Cs/AS15. Reversely, NH₄⁺ counter cation leads to the weakness of HPA acidity formed in HPA-NH₄/AS15 sample. The obtained result shows that Cs⁺ is more suitable than NH₄⁺ as counter cation of AS15 support's Brønsted site to prepare HPA/AS15 material.

The priority of Cs⁺ counter cation is also proved by the HPA leaching and catalytic stabilities. Fig. 9 and the data shown in Table S4 indicate that after five washing times with ethanol-water mixture, the HPA content of HPA-Cs/AS15 sample is inconsiderably changed (23.16 wt% at 1st and 22.57 wt% at 5th washing time). The HPA contents of HPA-NH₄/AS15 sample at 1st and 5th washing times are 24.28 wt% and 12.33 wt%, respectively. These results show that HPA-Cs/AS15 sample has better HPA leaching stability than HPA-NH₄/AS15 sample. Fig. 10 and the data shown in Table S5 demonstrate that after five reaction cycles, the conversions of the fructose fragrant synthesis over studied catalysts are reduced. The decrease of EAA conversion could be assigned to the loss of catalyst weight during the recovery from the ended reaction for the next cycle as shown in our previous study [29]. In addition, the decrease rate of the EAA conversion may be also explained by the loss of HPA immobilised on catalyst during the reaction. By the more stable HPA Brønsted immobilisation, HPA-Cs/AS15 sample shows a better catalytic stability at fifth reaction cycle compared with HPA-NH₄/AS15 sample. The EAA conversion over HPA-Cs/AS15 catalyst reduce 5.52 % (from 94.82 % at the first reaction cycle to 89.59 % at the fifth reaction cycle), lower than that over HPA-NH₄/AS15 catalyst (7.12 %). This result once again shows the advantage of Cs⁺ compared with NH₄⁺ for the HPA/AS15 preparation.

3.2.3. Effect of catalyst weight

The required catalyst amount for fructose fragrance synthesis depends on type and acidity of catalyst. The experimental results of different HPA-Cs/AS15 catalyst weights (2, 3 and 4 wt% to reactants total mass) shown in Fig. 11 and Table S6 indicate that in the case of using cyclohexane solvent, the sample with 3 wt% (HCA-3 wt%) is suitable for fructose fragrance synthesis (EAA conv. is 81.93 %). HCA-2 wt% has not enough active sites for the reaction (EAA conv. is 73.11 %). However, HCA-4 wt% has lower catalytic activity (EAA conv. is 78.86 %) than HCA-3 wt%. The lower catalytic activity of HCA-4 wt% sample may be explained by the aggregation when increases the catalyst weight from 3 to 4 wt%, resulting the reduction of active site number and catalytic activity of HPA-Cs/AS15 catalyst.

3.2.4. Effect of the catalyst on reaction conditions

The reaction conditions of fructose fragrance synthesis such as solvent type, EAA:EG reactants molar ratio and diols reactant type were evaluated by Yang et. al over heterogenised PTSA catalyst. The results showed that the suitable solvent was cyclohexane among three measured solvents of isooctane, toluene and cyclohexane. The best EAA:EG reactants molar ratio and diols reactant type were 1:1.5 and EG, respectively [4].

The results shown in Fig. 12-13 and Tables S7, S8 illustrate the agreement results of fructose fragrance synthesis over HPA-Cs/AS15 catalyst with that over heterogenised PTSA studied by Yang et. al in terms of EAA:EG reactants molar ratio (1:1.5) and diols reactant type (EG). This agreement is because these reaction conditions are not affected by the catalyst type. However, in term of solvent type, the obtained result of fructose fragrance synthesis over HPA-Cs/AS15 catalyst is different from that over heterogenised PTSA catalyst. The results shown in Fig. 14 and Table S9 indicate that toluene is the suitable solvent (EAA conv. is 95.58 %). Isooctane solvent is also a good solvent that has inconsiderably lower efficiency (EAA conv. is 94.82 %) in comparison to toluene solvent. The explanation for this result may be the boiling temperatures of the solvents. Among isooctane, toluene and cyclohexane solvents, cyclohexane has the lowest boiling temperature of 81.4 °C, toluene has the highest one of 110.6 °C, isooctane has the medium one of 99°C. For the refluxing, temperature of reaction needs to achieve the boiling point of solvent. HPA-Cs/AS15 is a mesoporous catalyst with the presence of HPA inside the pore system. A high temperature can promote the diffusion of the reactants into the pore system of HPA-Cs/AS15 catalyst to contact with immobilised HPA molecules. Because of this reason, the toluene and isooctane solvents should be the better candidates compared to cyclohexane solvent.

The good result obtained with isooctane solvent shows that the temperature arounds 100 °C may be good for fructose fragrance synthesis over HPA-Cs/AS15 catalyst.

3.2.5. Comparison study

Heterogenisation efficiency of the HPA-Cs/AS15 catalyst is further measured by catalytic comparison to those of pure HPA and the homogeneous strong acid catalysts (PTSA and H₂SO₄) in the fructose fragrance synthesis. Fig. 15 and the data shown in Table S10 demonstrate the positive result that HPA-Cs/AS15 catalyst shows better catalytic activity compared with commercial pure HPA catalyst. After 120 minutes of acetalisation, EAA conversion of fructose fragrance synthesis over commercial pure HPA is 89.52 %, lower than that over HPA-Cs/AS15 sample (94.82 %). The soluble property of commercial pure HPA in the EG polar reactant limits the contact of HPA with EAA reactant (which is much less polar than EG), therefore resulting the catalyst deactivation of this catalyst in fructose fragrance synthesis.

In comparison to H₂SO₄ and PTSA homogeneous catalysts, the performance of HPA-Cs/AS15 sample is higher than H₂SO₄ catalyst (EAA conv. is 91.43 %), but nearly equal to PTSA catalyst (EAA conv. is 94.44 %) in the fructose fragrance synthesis. PTSA is a strong organic acid. Therefore, it has high dispersibility in the reaction media to have ideal contact ability with the reactants, conducting the high catalytic performance of this catalyst for fructose fragrance synthesis. The results show that HPA-Cs/AS15 is an effective inorganic catalyst for fructose fragrance synthesis with the known advantages of heterogeneous catalysts.

4. Conclusions

The new HPA-Cs/AS15 was successfully prepared and applied as catalyst for the fructose fragrance synthesis. The obtained results proved that cesium ion was an effective counter cation of the ion-exchanged AS15 support (that was P123 structural chemically oxidatively removed) for preparing of HPA-Cs/AS15 material. This catalyst had high acidity (confirmed by NH₃-TPD spectrum), good immobilised HPA content (23.16 wt%), very good HPA leaching stability (the HPA lost content was only 2.55 % after five washing times) and high catalytic performance (the highest EAA conversion was 95.58 %, the activity reduced only 5.52 % after five reaction cycles, the better activity of HPA-Cs/AS15 than those of HPA-NH₄/AS15, pure HPA and H₂SO₄ homogeneous catalyst).

The use of HPA-Cs/AS15 catalyst did not affect the reaction conditions of the fructose fragrance synthesis such as EAA:EG reactants molar ratio and diols reactant type. The suitable solvent was not only depended on the reaction type, but also being affected by catalyst type. Toluene and isooctane which had the higher boiling temperatures than 100 °C were the suitable solvents in comparison to cyclohexane solvent (with the lower boiling temperature of 81.4 °C) for promoting the diffusion of the reactants into the mesopore system of HPA-Cs/AS15 catalyst to contact with the immobilised HPA molecules. The catalytic performance of HPA-Cs/AS15 catalyst in the fructose fragrance synthesis expected to open the catalytic potential of this catalyst for other organic synthesis reactions with polar reactant compounds.

Conflicts of interest

There are no conflicts to declare.

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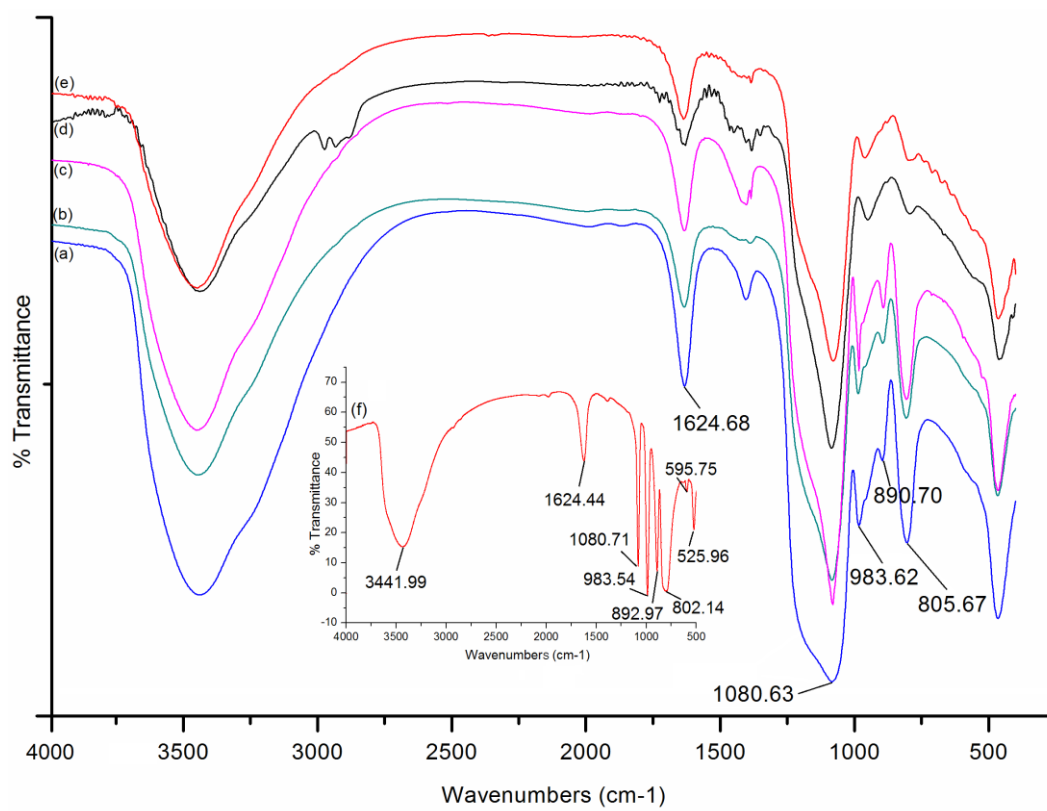


Fig. 1 FTIR spectrums of the samples: (a) HPA-NH₄/AS15-CAL; (b) HPA-Cs/AS15; (c) HPA-NH₄/AS15; (d) AS15-CAL; (e) AS15-OX; (f) HPA

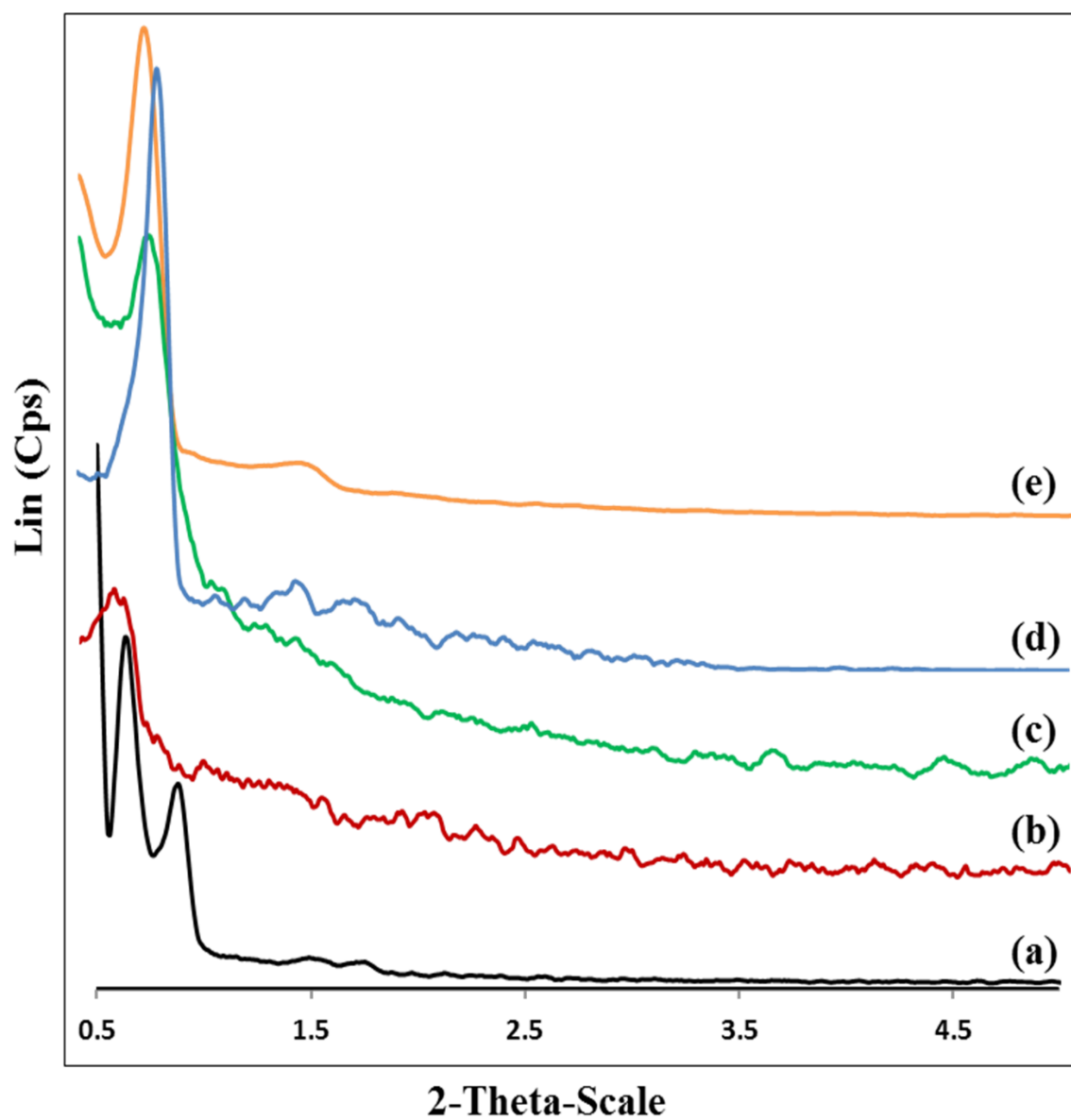


Fig. 2 SAXS patterns of the samples: (a) HPA-NH₄/AS15-CAL; (b) HPA-Cs/AS15; (c) HPA-NH₄/AS15; (d) AS15-CAL; (e) AS15-OX

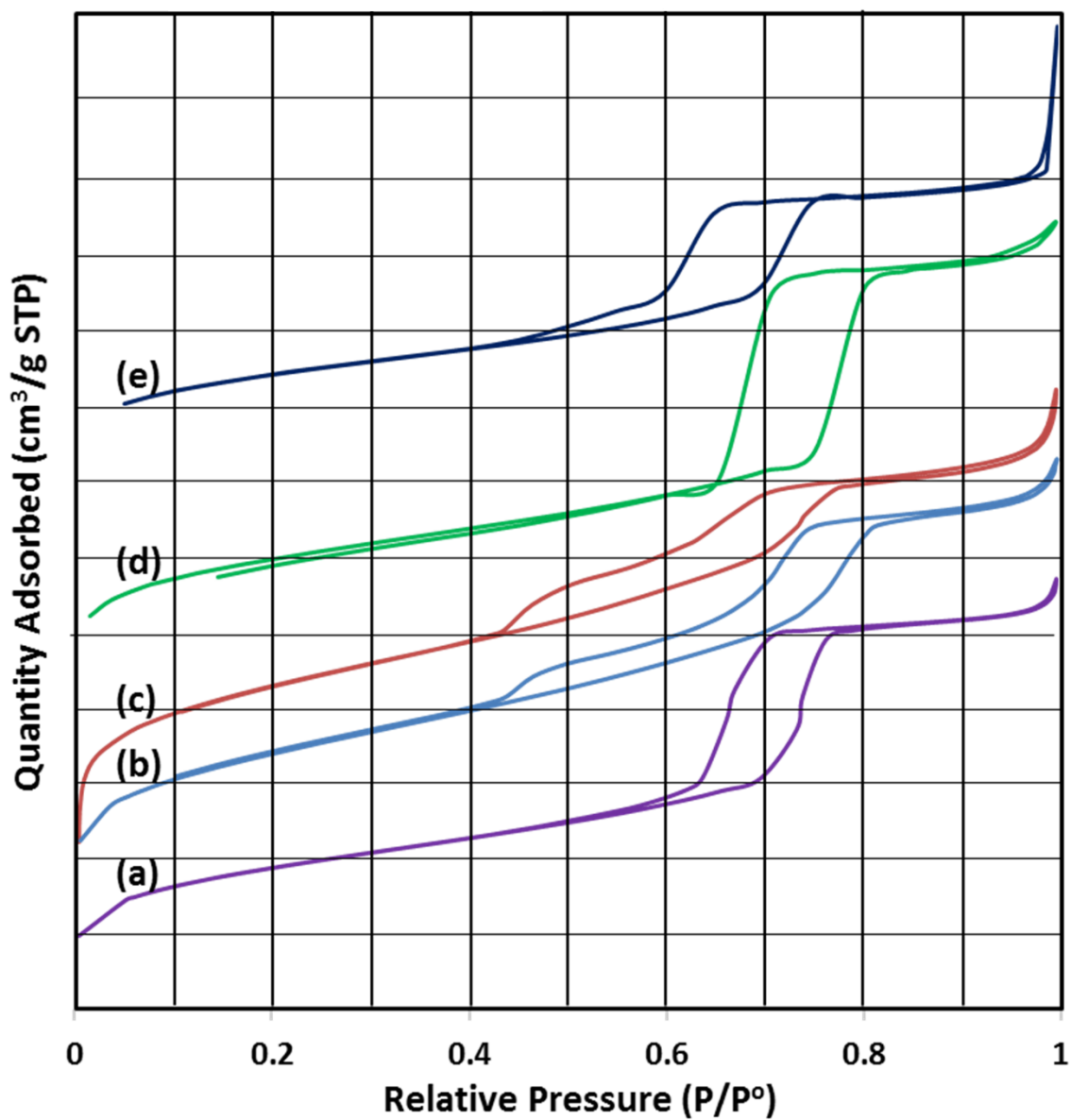


Fig. 3 Nitrogen adsorption and desorption isotherms of the samples: (a) HPA-NH₄/AS15-CAL; (b) HPA-Cs/AS15; (c) HPA-NH₄/AS15; (d) AS15-CAL; (e) AS15-OX

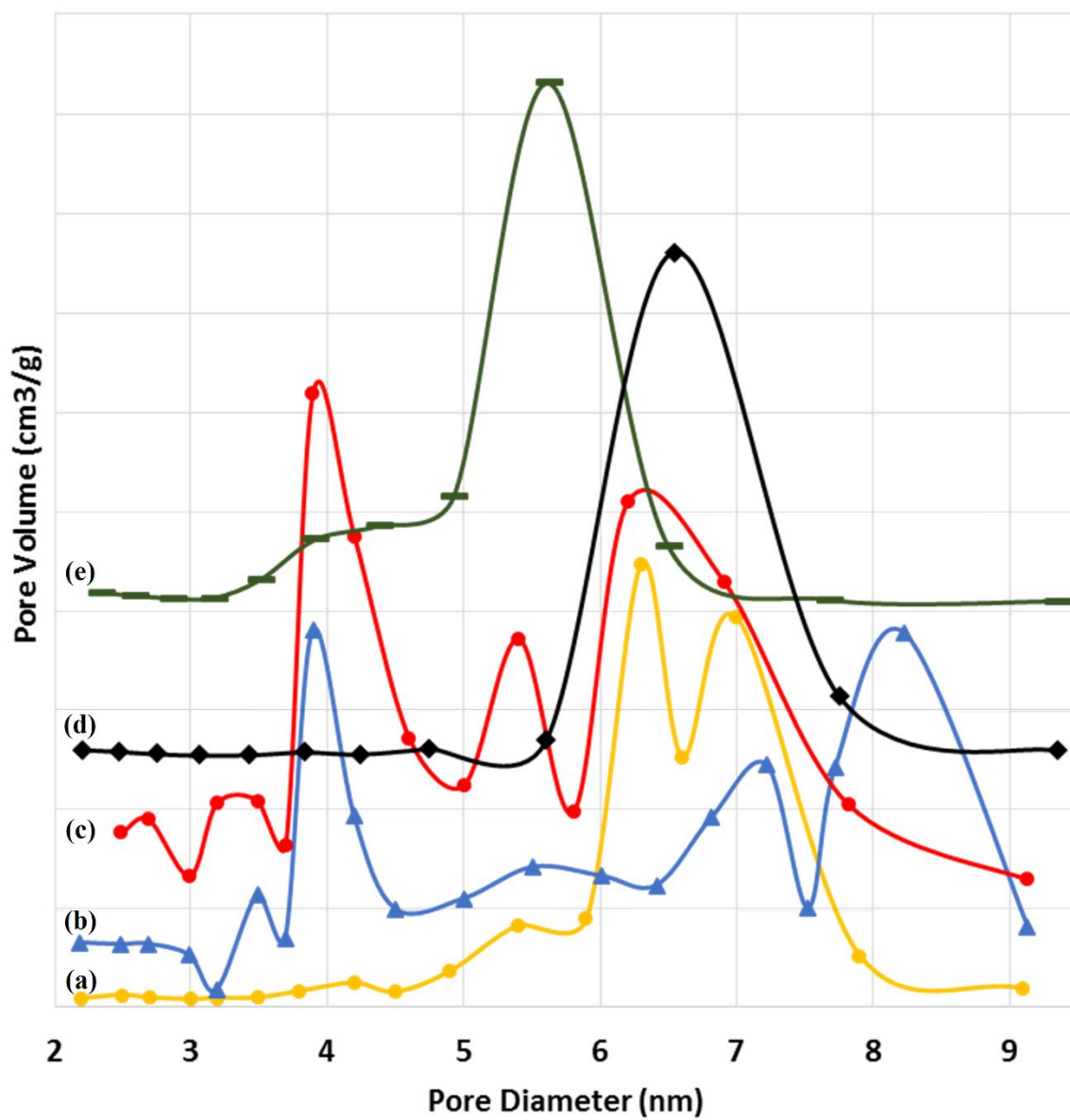


Fig. 4 Pore size distributions (BJH desorption) of the samples: (a) HPA-NH4/AS15-CAL; (b) HPA-Cs/AS15; (c) HPA-NH4/AS15; (d) AS15-CAL; (e) AS15-OX

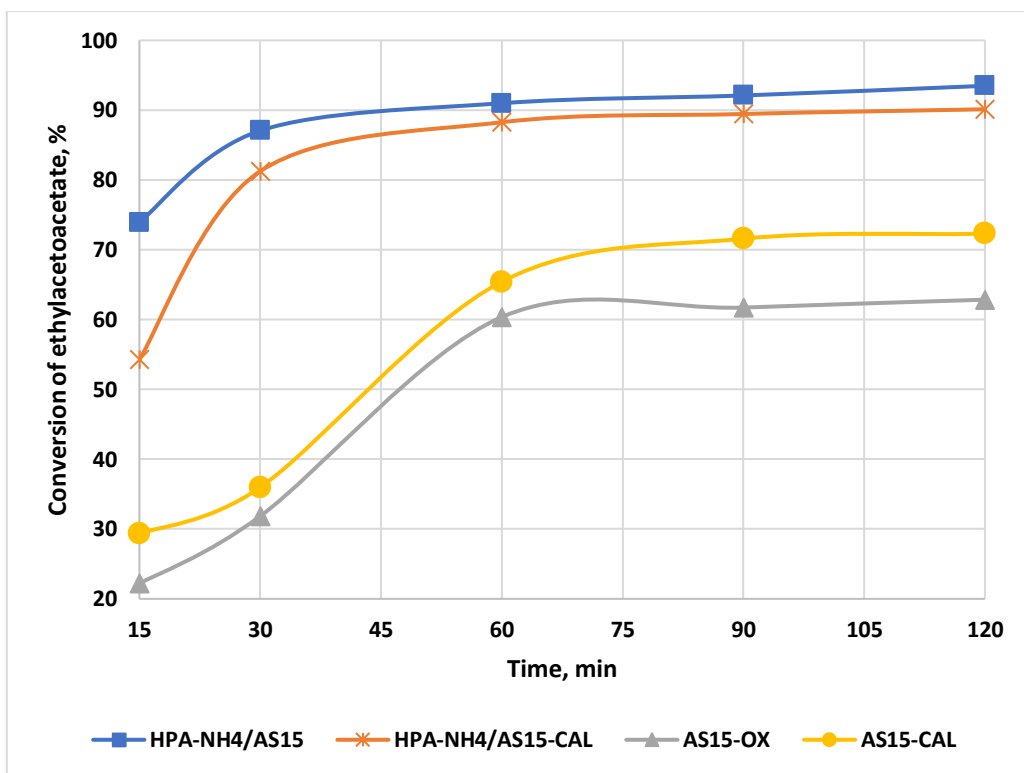


Fig. 5 Catalytic activities of the catalysts in fructose fragranciness synthesis under different support treatment conditions (other reaction conditions - catalyst weight: 3 wt%, solvent: isooctane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

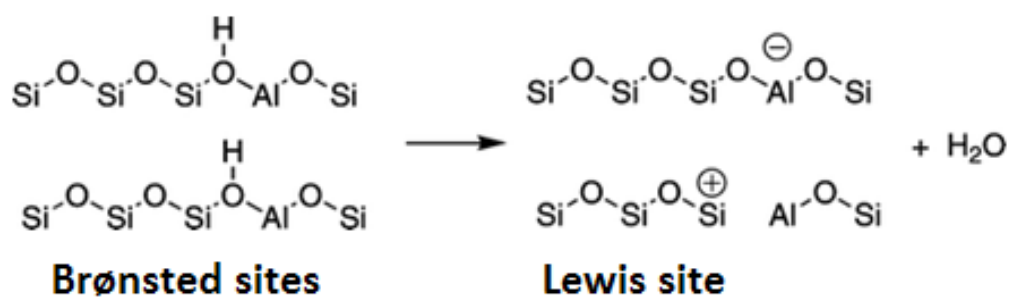


Fig. 6 The decomposition of Brønsted sites

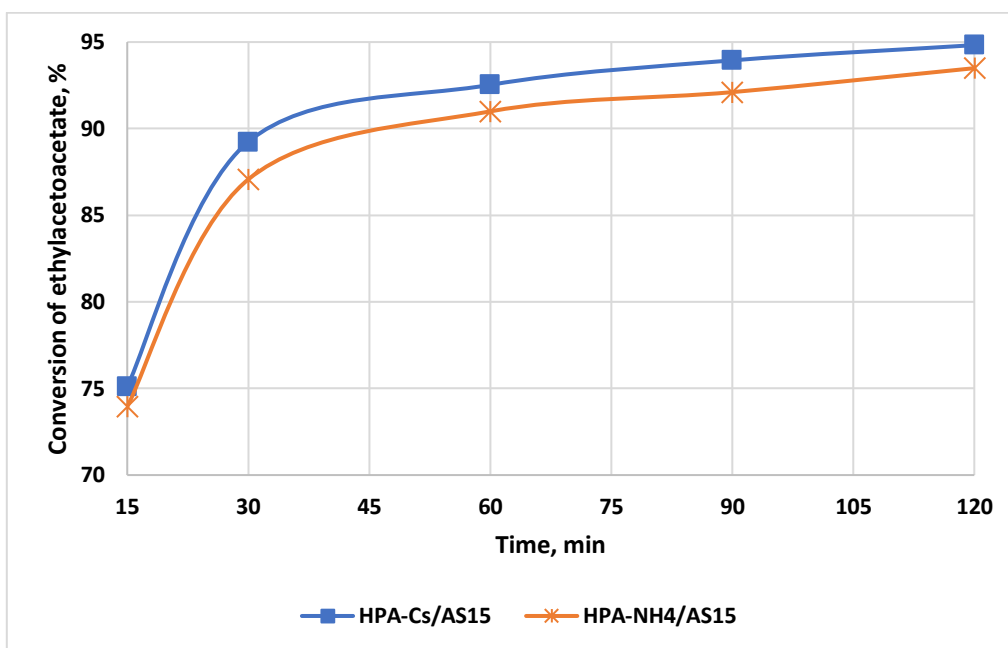


Fig. 7 Effect of counter cation type on the catalytic activities of the samples in fructose fragrant synthesis (other reaction conditions - catalyst weight: 3 wt%, solvent: isooctane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

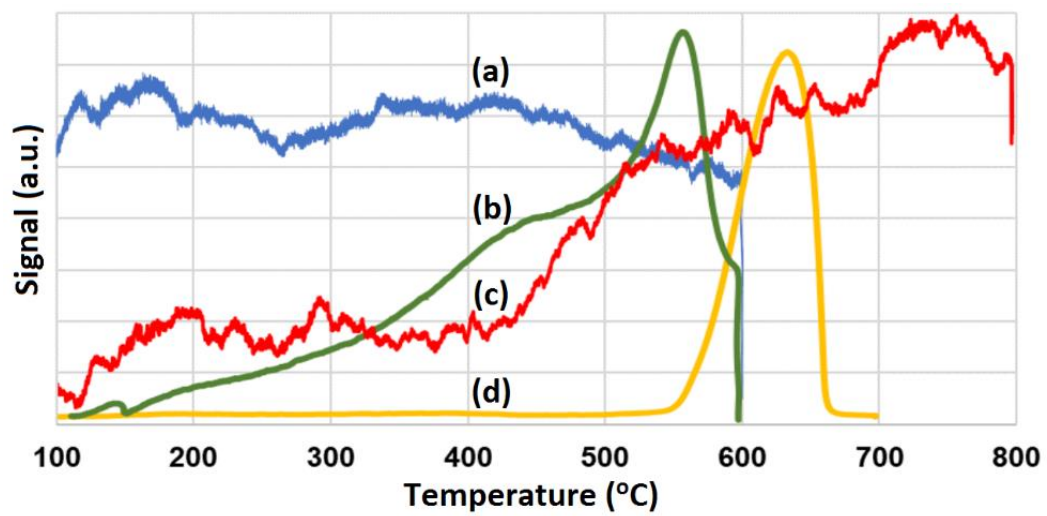


Fig. 8 NH₃-TPD spectrums of the samples (a) AS15-OX; (b) HPA-NH₄/AS15; (c) HPA-Cs/AS15; (d) Pure HPA

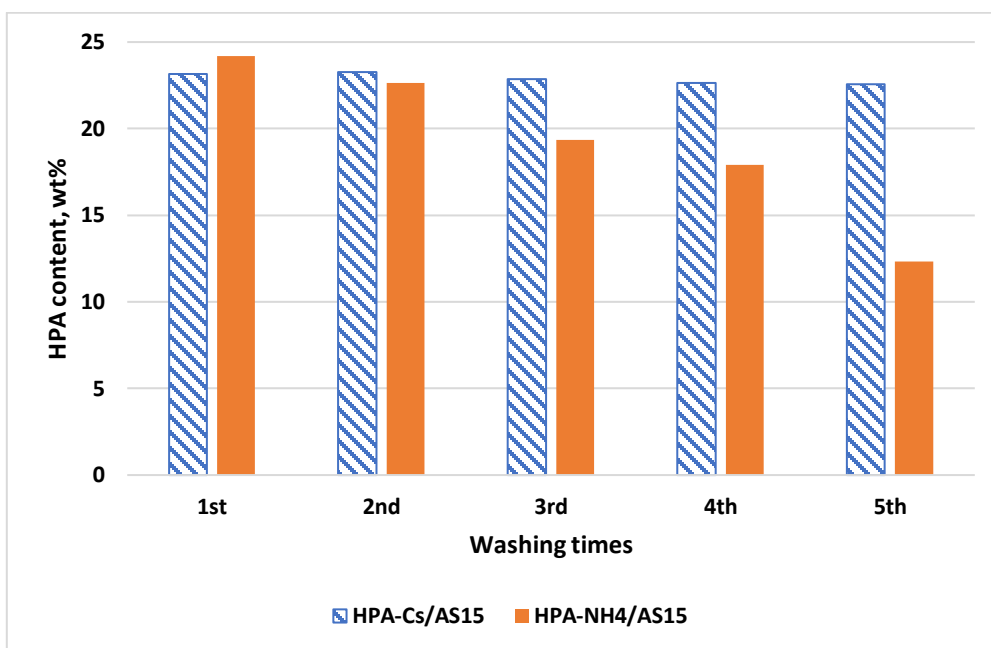


Fig. 9 HPA leaching stability on the AS15 support ion-exchanged with different counter cations

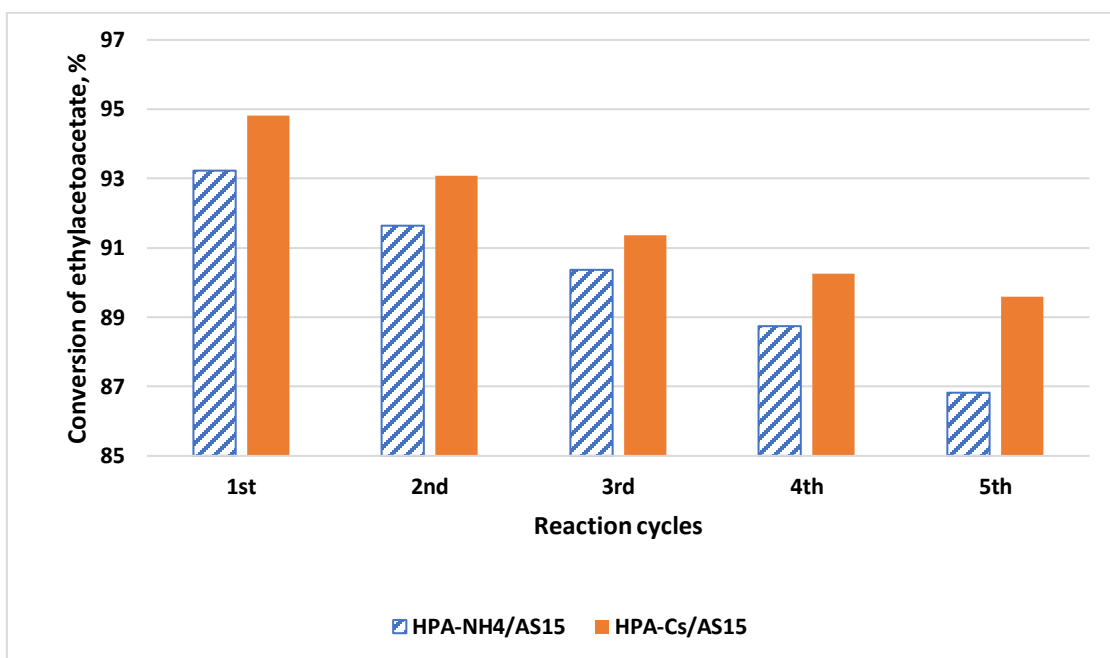


Fig. 10 Catalytic stability of HPA/AS15 samples that supports are ion-exchanged with different counter cations in fructose fragrant synthesis

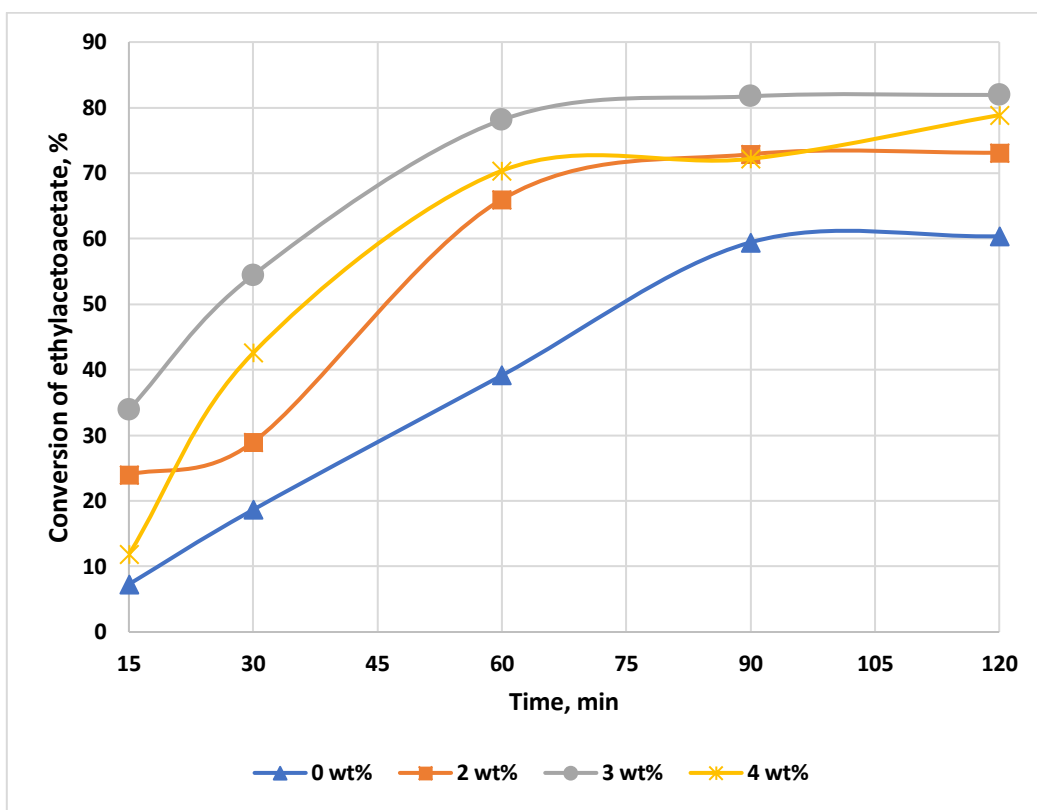


Fig. 11 Catalytic activity of HPA-Cs/AS15 by catalyst weight in fructose fragranciness synthesis (other reaction conditions - solvent: cyclohexane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

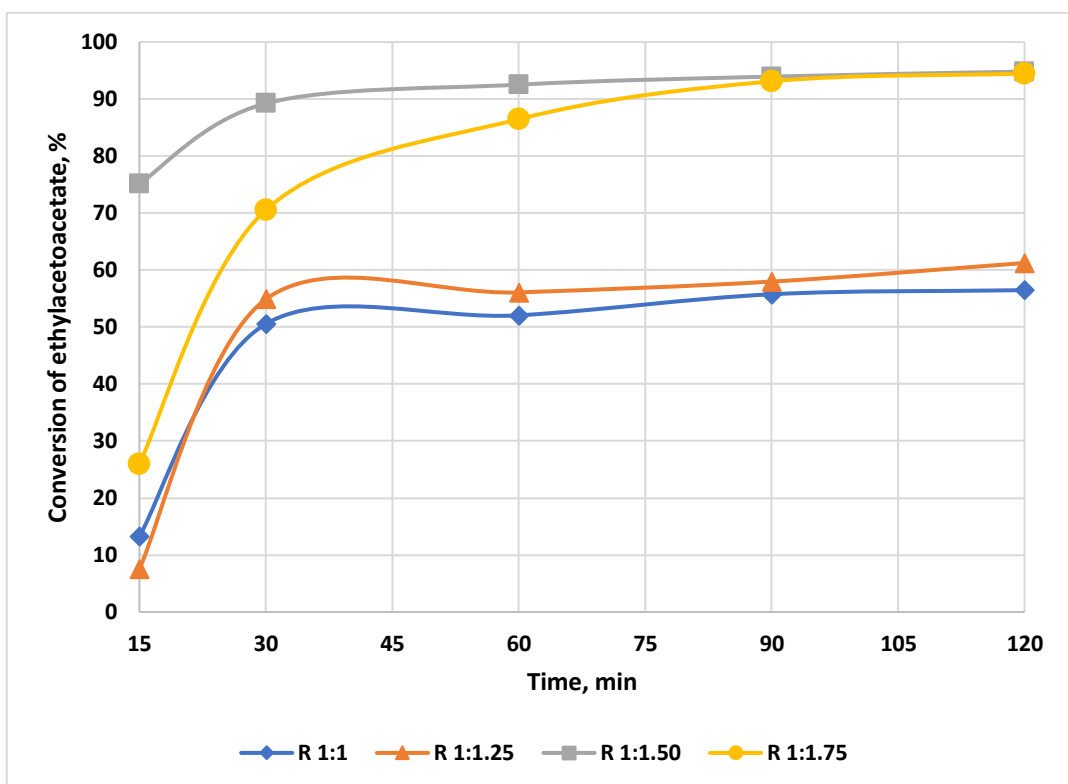


Fig. 12 Catalytic activity of HPA-Cs/AS15 by different EAA:EG reactants molar ratios in fructose fragrant synthesis (other reaction conditions - catalyst weight: 3 wt%; solvent: isooctane; diols reactant: EG)

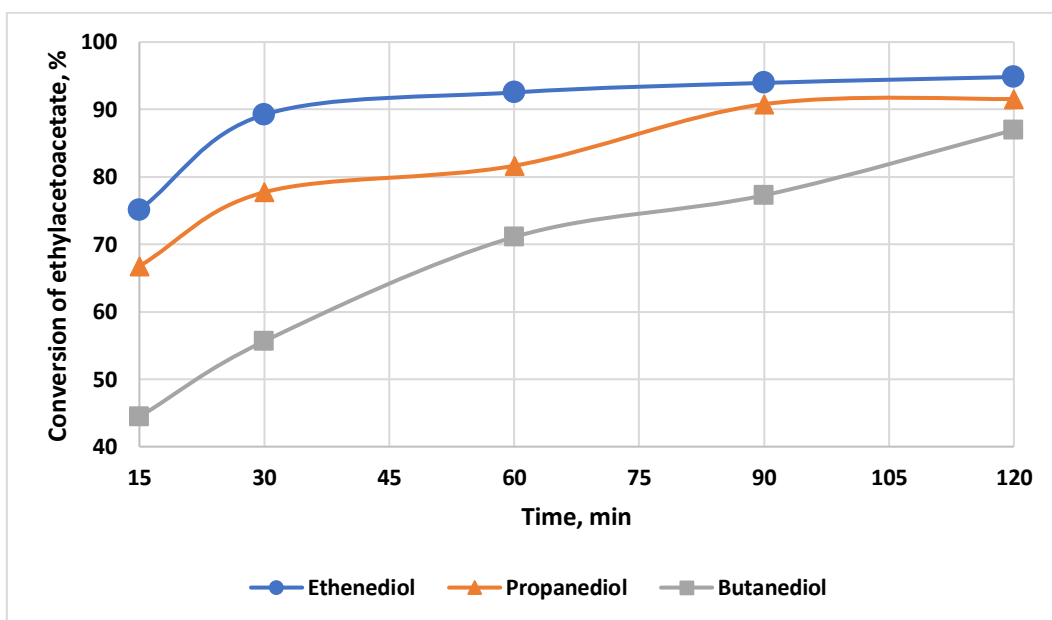


Fig. 13 Catalytic activity of HPA-Cs/AS15 by different reactant type in fructose fragrant synthesis (other reaction conditions - catalyst weight: 3 wt%; solvent: isooctane; reactants molar ratio of EAA:EG = 1:1.5)

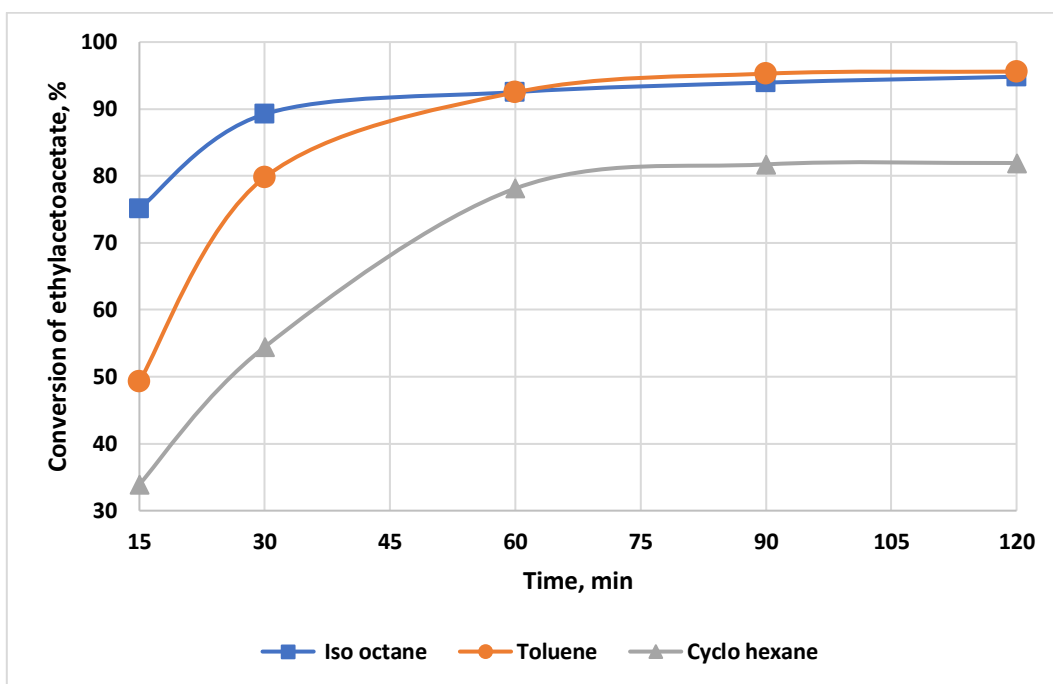


Fig. 14 Catalytic activity of HPA-Cs/AS15 by different solvent in fructose fragranciness synthesis (other reaction conditions - catalyst weight: 3 wt%; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

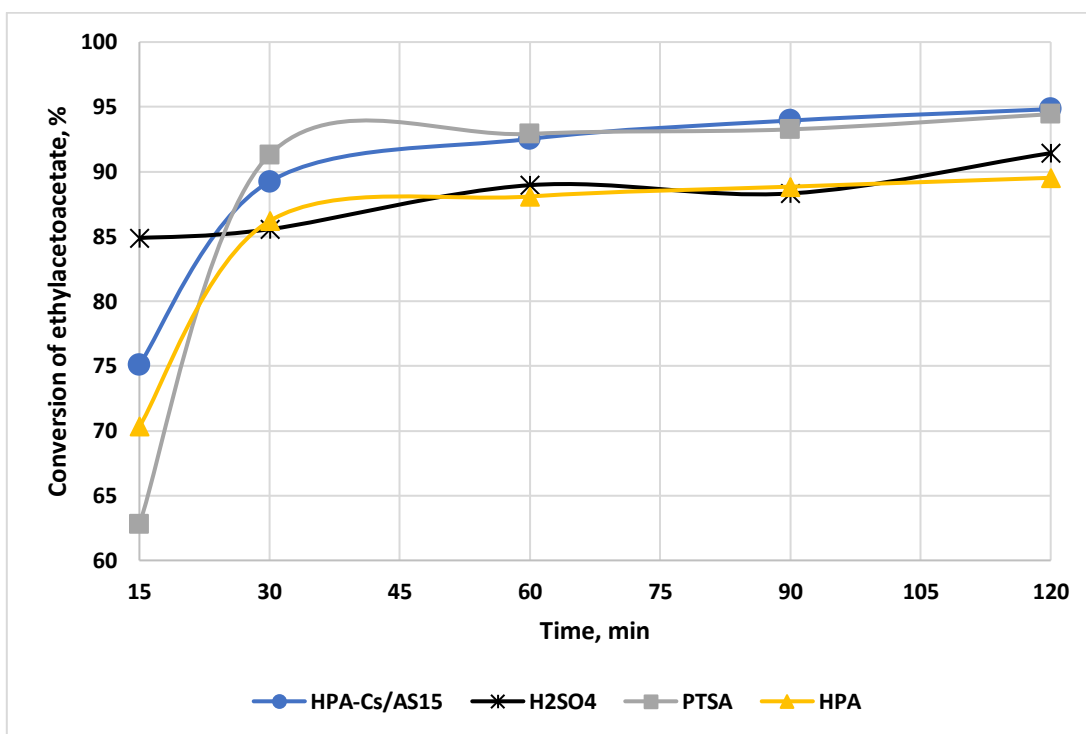


Fig. 15 Catalytic activity of HPA-Cs/AS15 compared to some homogeneous catalysts in fructose fragrance synthesis (other reaction conditions – solvent: isooctane; reactants molar ratio of EAA:EG = 1:1.5; diols reactant: EG)

Table 1 The prepared HPA/AS15 samples

Sample	P123 degradation method		Counter cation	
	Thermal treatment	Oxidation	NH ₄ ⁺	Cs ⁺
HPA-NH ₄ /AS15-CAL	x		x	
HPA-NH ₄ /AS15		x	x	
HPA-Cs/AS15		x		x

Table 2 BET data of the samples

Sample	S_{BET}, m²/g	Average D_{pore}, nm	V_{pore}, cm³/g
AS15-CAL	786	6.54	0.96
AS15-OX	750	5.10	0.93
HPA-NH ₄ /AS15-CAL	628	5.28	0.86
HPA-NH ₄ /AS15	603	5.05	0.59
HPA-Cs/AS15	591	5.57	1.22

Table 3 HPA contents of HPA/AS15 catalysts by EDX

Sample	HPA content, wt%
HPA-NH ₄ /AS15-CAL	17.81
HPA-NH ₄ /AS15	24.28
HPA-Cs/AS15	23.16